



Ultrahigh-permeance PIM-1 based thin film nanocomposite membranes on PAN supports for CO₂ separation

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ABSTRACT

High permeance membranes were produced by addition of highly permeable nanoparticulate fillers (hypercrosslinked polystyrene, HCP, and its carbonized form, C-HCP) to a high free volume polymer (polymer of intrinsic microporosity PIM-1) in a thin film (typically 2 μm) on a porous polyacrylonitrile support. Self-standing mixed matrix membranes (MMMs) of thicknesses in the range 40–90 μm were also prepared with the same polymer and fillers. While robust MMMs could only be formed for moderate filler loadings, thin film nanocomposite (TFN) membranes could be produced from dispersions with filler loadings up to 60 wt%. On increasing the filler loading, CO₂ permeance increased in line with the predictions of the Maxwell model for a highly permeable filler. Physical ageing led to some loss of permeance coupled with an increase in CO₂/N₂ selectivity. However, for TFN membranes the greatest effects of ageing were seen within 90 days. After ageing, TFN membranes showed high permeance with reasonable selectivity; for example, with 60 wt% C-HCP, CO₂ permeance > 9300 GPU, CO₂/N₂ selectivity ~ 11.

1. Introduction

Capture of CO₂ from the exhaust of a combustion process can help to mitigate climate change [1,2]. Captured CO₂ can be stored to reduce carbon footprint or serve as an alternative source of carbon for the synthesis of diverse chemicals and fuels (methanol, carboxylic acids, carbonates, polycarbonates, etc.) [3–5]. In recent years, membrane-based processes have emerged as attractive candidates for energy-efficient separations [6–10]. The productivity of a membrane can be expressed in terms of (i) flux, the amount of permeate passing through unit membrane area in unit time, (ii) permeance, the flux normalized for the pressure gradient, or (iii) permeability, the permeance normalized for the membrane thickness. Permeability may be regarded as a property of the membrane material. In general, high selectivity can only be achieved by compromising on permeability and vice versa [11], as demonstrated elegantly by Robeson [12]. However, Merkel et al. [13] have shown that, under practical conditions for post-combustion carbon capture, higher permeance dominates the economics of the separation process. High selectivity and low permeance necessitates a very large membrane area, which makes it a cost-ineffective process.

Permeance can easily be increased by selecting very thin

membranes. However, very thin films are not sufficiently robust for practical use without a highly porous support, which may be of the same material (integrally skinned asymmetric membrane) or of a different material (thin film composite, TFC, membrane). Hägg et al. reported highly selective polyvinyl amine (PVAm) based TFC membranes (selectivity, $\alpha(\text{CO}_2/\text{N}_2) = 50\text{--}500$) [14–16]. MTR Inc. and Qiao et al. independently reported membranes with moderate selectivity ($\alpha \sim 20\text{--}50$) but with much higher permeance (up to ~ 4000 GPU) [13,17,18]. There is a drive to develop even higher permeance membranes that maintain their performance over time.

High-free-volume glassy polymers, such as polymers of intrinsic microporosity (PIMs) or poly[1-(trimethylsilyl)-1-propyne] (PTMSP), are highly permeable to gases such as CO₂ and demonstrate reasonable gas selectivity, making them attractive materials for gas separation membranes [19–22]. A body of work has demonstrated that the addition of fillers into these materials, to form mixed-matrix membranes (MMMs), can increase permeability many fold, as well as reducing the effects of physical ageing [11,23–26]. However, most research into MMMs has been conducted on relatively thick, self-standing membranes (40–100 μm), which show poor flux due to their thickness. Furthermore, many studies of MMMs have used fillers composed of

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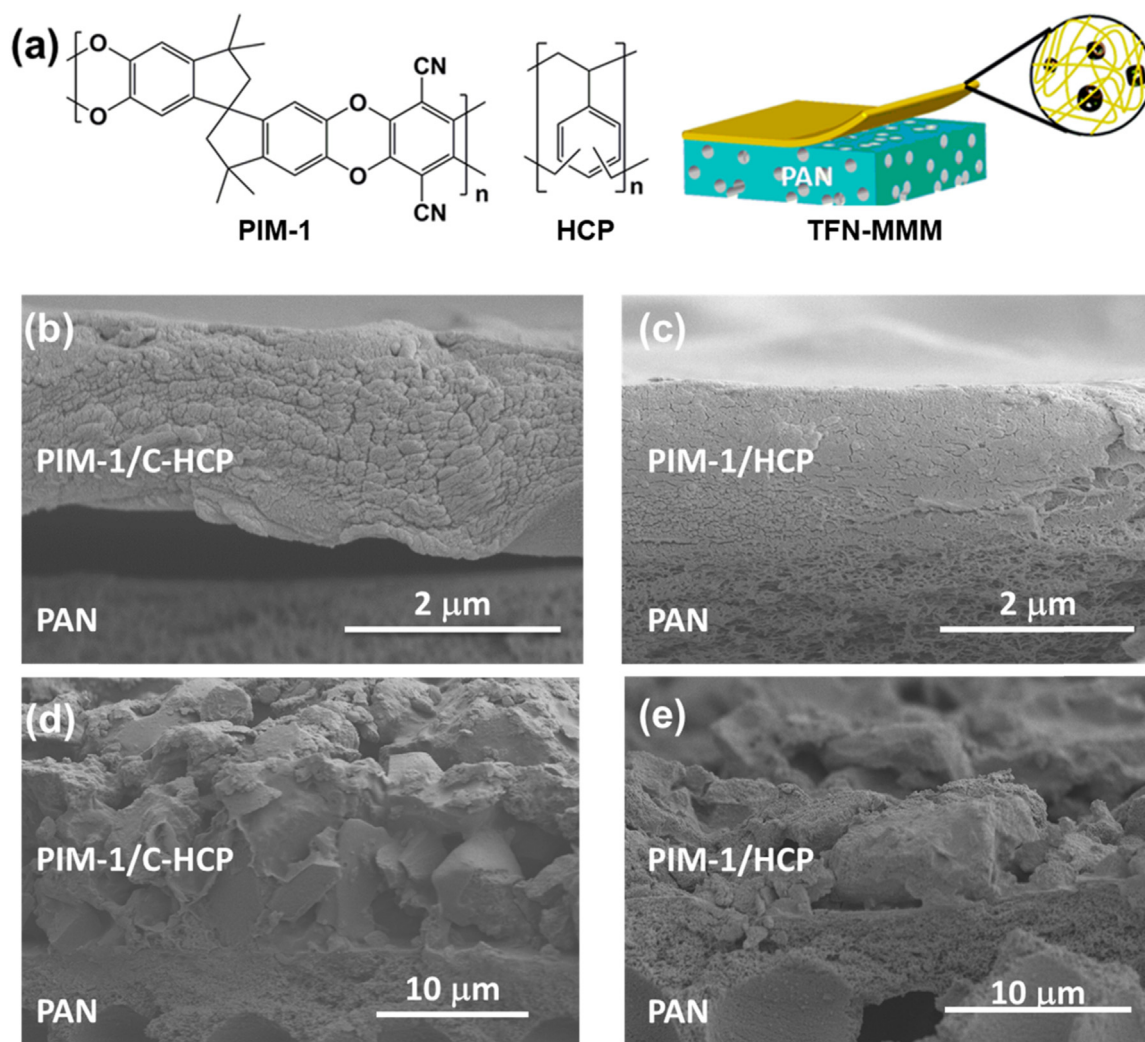


Fig. 1. (a) Molecular structures of PIM-1 and HCP, and schematic illustration of a thin-film nanocomposite membrane, with a selective layer of PIM-1 with nanoparticulate HCP or C-HCP filler, on a highly porous PAN support. SEM images of (b, d) thin film nanocomposite of PIM-1/C-HCP and (c, e) thin film nanocomposite of PIM-1/HCP. The images shown in (b) and (c) represent lower filler concentration (10 wt%), whilst those in (d) and (e) represent higher filler concentration (60 wt %).

relatively large particles ($> 1 \mu\text{m}$), which could bridge the entire thickness of a very thin film. We have previously reported the performance of MMMs of hypercrosslinked polystyrene (HCP) nanoparticles (diameter *ca.* 55 nm) in the polymer of intrinsic microporosity PIM-1 [11]. Here, we extend that work to thin film nanocomposite (TFN) membranes with a thin coating of mixed-matrix material on a porous polyacrylonitrile (PAN) support, utilizing both HCP nanoparticles and carbonized HCP (C-HCP) nanoparticles as fillers (Fig. 1).

2. Experimental

2.1. Materials

Dimethylacetamide (DMAc), toluene, methanol, potassium hydroxide, chloroform, vinylbenzyl chloride, p-divinylbenzene, sodium dodecyl sulphate, potassium persulphate, diethyl ether, 1,2-dichloroethane (DCE) and ferric chloride (FeCl_3) were purchased from Sigma-Aldrich and used as received. Tetrafluoroterephthalonitrile (TFTN, 98%, Aldrich) was purified by sublimation; it was heated to around 150°C and the pure product collected without vacuum. 5,5',6,6',-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (THSBI, 98%, Alfa Aesar) was dissolved in methanol and re-precipitated from dichloromethane before use. Anhydrous potassium carbonate

(K_2CO_3 , 99.0%, Fisher) was dried in an oven at 110°C overnight before use. Porous polyacrylonitrile (PAN) membrane (Sepro PA350 ultra-filtration membrane) was kindly provided by Prof. Ingo Pinnau, King Abdullah University of Science and Technology, Saudi Arabia.

2.2. Synthesis of PIM-1, HCP nanoparticles and carbonized HCP nanoparticles

PIM-1 and hypercrosslinked polystyrene (HCP) nanoparticles were synthesized as reported previously and details are summarized in the Supporting information [11,27]. Carbonization of HCP nanoparticles (carbonized product referred to as C-HCP) followed a previously reported procedure [28]: 0.5 g of HCP and 2 g of potassium hydroxide were mixed using a mortar and pestle. The mixture was then transferred to an alumina boat and the boat was placed in an oven. The temperature of the oven was raised to 800°C at a rate of 5°C min^{-1} . The oven temperature was then maintained at 800°C for 2 h under a gentle N_2 flow. The oven was then allowed to cool to ambient temp. The dark mass was washed with 1 L water, followed by 200 mL methanol. It was then dried at 100°C under vacuum.

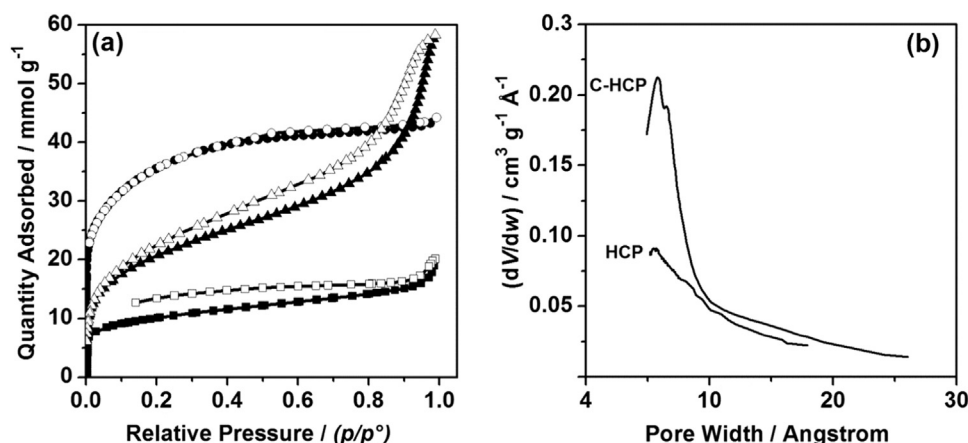


Fig. 2. (a) Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K for PIM-1 (■, □), HCP (▲, △) and C-HCP (●, ○). (b) Pore size distributions for HCP and C-HCP determined from N₂ adsorption data by the Horvath-Kawazoe method.

2.3. Gas sorption analysis

Nitrogen adsorption and desorption isotherms at 77.3 K and 298 K, and CO₂ adsorption and desorption isotherms at 298 K, were measured using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Samples were degassed offline at 60 °C for 12 h under vacuum (10⁻⁵ bar) before analysis, followed by degassing on the analysis port under vacuum.

2.4. Membrane preparation

TFN membranes of PIM-1/HCP and PIM-1/C-HCP on PAN supports were prepared by dip coating with 3% w/v total solids in chloroform (CHCl₃). Coating solutions were prepared with four different proportions of filler to total solids (10, 20, 40 and 60 wt%). For example, for 10 wt% filler, a suspension of filler (0.03 g) in 5 mL CHCl₃ was stirred for 12 h at ambient temperature, followed by sonication for 30 min in a Bandelin Sonorex ultrasonic bath at ambient temperature. A solution of PIM-1 (0.27 g in 5 mL CHCl₃) was added to the suspension and stirred for 20 h. The resulting solution was sonicated for 20 min in an ultrasonic bath at ambient temperature before being used for dip coating. A PAN support was dried under vacuum at ambient temperature for 1 h, then a piece (63 × 45 mm) was fixed on a glass slide and the edge sealed with aluminium tape, to ensure only the PAN-coated side of the support came into contact with coating solution. The glass slide was then dipped vertically into a tray filled with coating solution. It was kept immersed for 2 s at ambient temperature, and then removed slowly. The TFN membranes were rested on a horizontal surface for 24 h and then kept in a vacuum desiccator for 2 h, in order to remove the residual solvent. It is known that membrane performance depends on drying parameters, as demonstrated previously [29–31]. For better comparison with previous work, all the membranes were dried at room temperature. Self-standing MMM membranes were prepared by the solution casting method as reported previously [11] and described in the supporting information.

2.5. Membrane characterization

The average pore size of the PAN membrane was measured by a Porolux™ 1000 Porometer. The membrane morphology was studied by scanning electron microscopy (SEM) using a Hitachi S-4800 Field-Emission Scanning Electron Microscope with Energy Dispersive X-Ray (EDX) detector and cold cathode electron source. The membrane cross section was prepared via freeze fracturing using liquid nitrogen. The sample was then coated with gold by sputtering using an Emitech coater.

2.6. Gas permeation measurements

The permeability measurements using pure gases (CO₂ and N₂) were carried out by the standard variable volume method [32] (see Supporting information) at an upstream gas pressure of 2 atm and at ambient temperature (~298 K), while maintaining the permeate side at the atmospheric pressure. Membrane samples (2.5 cm in diameter), after removing from the vacuum desiccator, were immediately mounted in the permeation cell. For ageing analysis, all the membranes were stored in a sealed petri dish at room temperature. The CO₂ and N₂ pure gas permeability after ageing was carried out at 2 atm upstream pressure and at ambient temperature. The gas permeance was calculated using Eq. (1):

$$K = \frac{Q}{tA(p_1 - p_2)} \cdot 10^{-6} \quad (1)$$

where K is the permeance in gas permeation units (1 GPU = 10⁻⁶ cm³[STP] cm⁻² s⁻¹ cmHg⁻¹ = 3.348 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹), Q is the volume of permeated gas (cm³, adjusted to STP [0 °C, 1 atm]), t is the permeation time (s), A is the membrane area (cm²), and p_1 and p_2 are the feed and permeate side pressures (cmHg), respectively. Gas permeability was calculated using Eq. (2):

$$P = \frac{Ql}{tA(p_1 - p_2)} \cdot 10^{-10} \quad (2)$$

where l is the membrane thickness (cm) and P is the permeability coefficient expressed in barrer (1 barrer = 10⁻¹⁰ cm³[STP] cm cm⁻² s⁻¹ cmHg⁻¹ = 3.348 × 10⁻¹⁶ mol m m⁻² s⁻¹ Pa⁻¹).

3. Results and discussion

3.1. Fillers for TFN membranes

We investigated two highly porous nanoparticulate fillers, a hypercrosslinked polystyrene (HCP) and its carbonised version (C-HCP). These fillers are easily prepared using inexpensive starting materials [11,28]. Fig. 2(a) compares the N₂ adsorption/desorption isotherms at 77 K for PIM-1, HCP and C-HCP. The polymer and fillers exhibit high uptake at low relative pressure, characteristic of a microporous material as defined by IUPAC (pore size < 20 Å) [33]. N₂ uptakes increase in the sequence PIM-1 < HCP < C-HCP, reflected in Brunauer–Emmett–Teller (BET) surface areas of 790, 1750 and 2700 m² g⁻¹ for PIM-1, HCP and C-HCP, respectively. Micropore volumes of the fillers were estimated from the N₂ adsorption isotherms. As generally observed for microporous polymers, the adsorption isotherms exhibit a positive slope in the relative pressure range 0.4–0.8, which may be attributed to swelling by the penetrant. We therefore extrapolated these data linearly to zero relative pressure to obtain an estimate of the

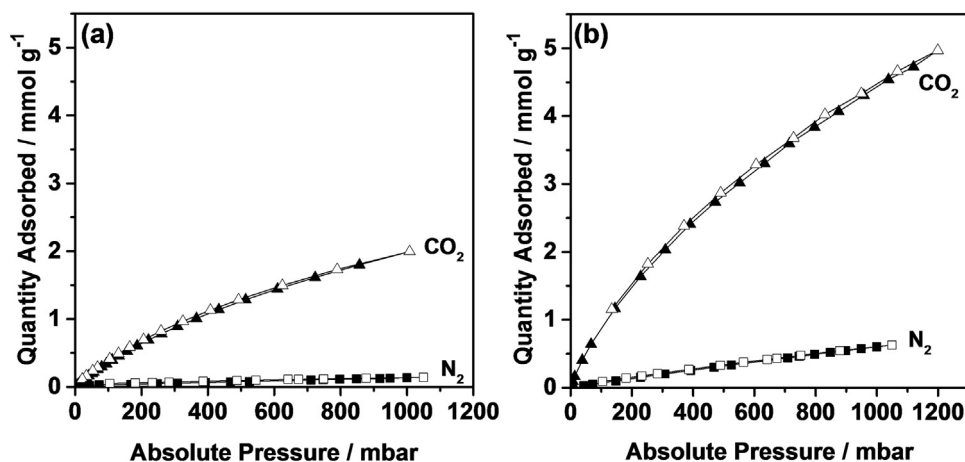


Fig. 3. CO₂ and N₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 298 K for (a) HCP and (b) C-HCP nanoparticles.

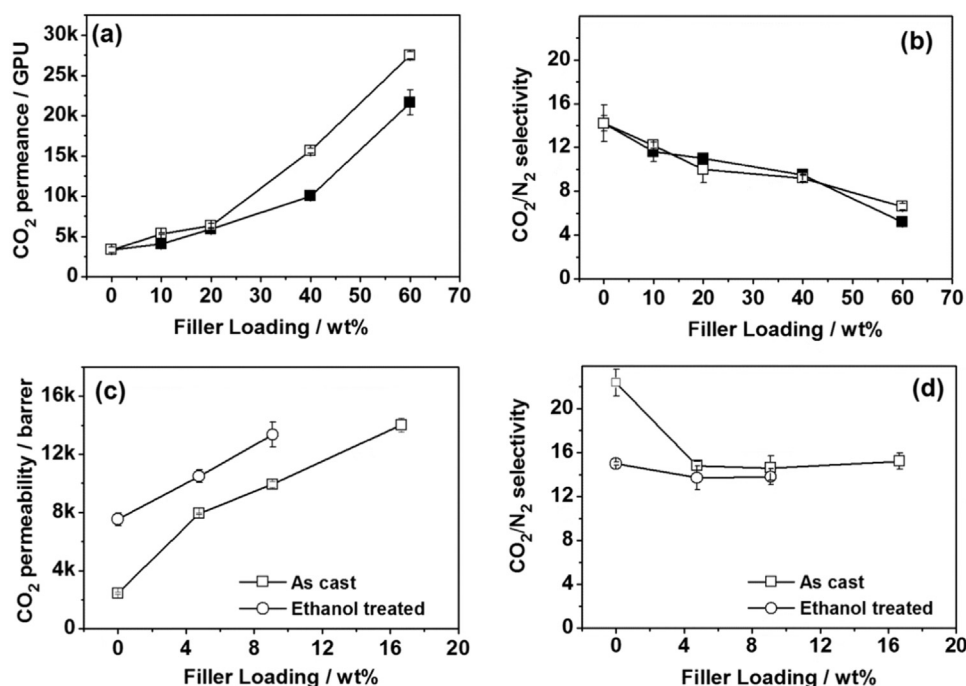


Fig. 4. Dependence of (a) CO₂ permeance and (b) CO₂/N₂ selectivity for TFN membranes (solid symbol represents PIM/HCP TFN membranes and open symbol represents PIM/C-HCP TFN membranes). Dependence of (c) CO₂ permeability and (d) CO₂/N₂ selectivity for self-standing as cast and ethanol treated PIM-1/C-HCP MMMs. All data are shown for non-aged membranes. Error bar represents the standard deviation of 3 samples. The CO₂ permeability and CO₂/N₂ selectivity for PIM-1/HCP MMMs were reported previously [11].

uptake of N₂ that can be attributed to the porosity of the filler. Hence, the bulk densities were evaluated as 0.65 g cm⁻³ for HCP and 0.57 g cm⁻³ for C-HCP, taking the skeletal densities to be those for polystyrene (1.05 g cm⁻³ [34]) and graphite (2.26 g cm⁻³ [35]), respectively. For HCP, this is within the range of densities previously reported for similar materials (0.35 [36], 0.78, 0.42 [37]). Analysis of the low pressure region of the adsorption isotherms by the Horvath-Kawazoe method [38] (Fig. 2(b)) indicates a higher level of ultramicroporosity (pore size < 7 Å) in C-HCP than in HCP. The combination of small pore size and high porosity makes these fillers interesting candidates for nanocomposite membranes.

Fig. 3 shows CO₂ and N₂ adsorption/desorption isotherms at 298 K. After carbonization, the CO₂ uptake is more than double that of HCP, reflecting the higher level of ultramicroporosity in C-HCP [39]. The higher CO₂ adsorption is helpful to improve the CO₂ permeability, as permeability depends on sorption and diffusivity [40]. The HCP particles retain their nanoparticulate morphology after carbonization (see Supporting information). The thermal stabilities were investigated by thermogravimetric analysis (see Supporting information). Thermal stability was improved by carbonization, the C-HCP showing only a

small weight loss up to 800 °C under N₂.

3.2. TFN membranes

TFN membranes were prepared by dip-coating a PAN support (thickness 150 μm; pore size ~ 31 nm with a narrow distribution, see Supporting information) with a dispersion of the filler in a solution of PIM-1 in chloroform. For comparison, self-standing MMMs with thicknesses in the range 40–90 μm were also prepared, by casting on a glass mould. TFN membranes could be prepared from coating solutions with ~ 60 wt% filler loading, while with self-standing MMMs the filler could be loaded only up to 17 wt%. After ethanol treatment, at higher C-HCP loading in a self-standing membrane, a very brittle and curly membrane was formed (see Supporting information). This membrane was difficult to handle and hence could not be analysed. The filler becomes the dominant phase in terms of volume fraction at loadings above 38 wt% for HCP and 35 wt% for C-HCP, taking the bulk densities for HCP, C-HCP and PIM-1 to be 0.65, 0.57 (see above) and 1.056 [41], respectively. Images from scanning electron microscopy (SEM) of TFN membranes at low and high loading are included in Fig. 1. A well-defined

thin ($\sim 2\ \mu\text{m}$) film with a homogeneous distribution of filler was achieved at low filler loadings, but at high loadings an irregular layer of varying thickness was formed. Apparent thicknesses of the selective layer from SEM images of TFN membranes are given in the [Supporting information](#).

3.3. Gas permeation analysis

3.3.1. Effect of filler loading on permeance and selectivity

Fig. 4a shows how CO_2 permeance varies with filler loading for unaged PIM-1/HCP and PIM-1/C-HCP TFN membranes (see [supporting information](#) for tabulated data). Both fillers give a marked increase in permeance with increase in filler loading, showing increases compared to pristine PIM-1 of up to $\sim 550\%$ with HCP and $\sim 725\%$ with C-HCP, in accordance with the high porosity and high internal surface area of HCP, and even higher values for C-HCP, as seen in Fig. 2. For comparison, Fig. 4c shows the variation of CO_2 permeability with filler loading for self-standing PIM-1/C-HCP MMMs, both “as cast” and after ethanol-treatment. Equivalent data for PIM-1/HCP MMMs have been reported previously [11]. It should be noted that self-standing, “as cast” MMMs with C-HCP show a higher increase in CO_2 permeability ($\sim 475\%$ at 17 wt% filler) than previously reported MMMs with HCP ($\sim 277\%$) [11], demonstrating the benefit of carbonized filler for improving gas permeability.

The effect of filler loading on CO_2/N_2 selectivity is shown in Fig. 4b for PIM-1/HCP and PIM-1/C-HCP TFN membranes, and in Fig. 4d for self-standing, “as cast” PIM-1/C-HCP MMMs. For TFN membranes, the dramatic increase in permeance on addition of filler is accompanied by a significant drop in selectivity. This could be due to the presence of microvoids in the selective layer, arising from poor packing of the filler or poor adhesion with the polymer matrix. Microvoids may provide high permeability pathways for both gases. Selectivity improves on ageing the membrane, as discussed later.

A number of models may be employed to describe the permeation of gases through a composite comprising a dispersed filler in a continuous matrix. One of the simplest is the Maxwell model, which was originally

developed for electrical conductivity [42], but can equally be applied to gas permeation [43]. The effective permeability of a mixed matrix membrane, P_{MMM} , depends on the volume fraction of the dispersed phase, Φ_d , and on the permeabilities of the dispersed and continuous phases, P_d and P_c , respectively, according to:

$$P_{\text{MMM}} = P_c \left[\frac{P_d + 2P_c - 2\Phi_d(P_c - P_d)}{P_d + 2P_c + \Phi_d(P_c - P_d)} \right] \quad (3)$$

Two limiting cases may be considered. At one extreme, if the dispersed phase is completely impermeable ($P_d = 0$), the Maxwell equation simplifies to

$$P_{\text{MMM}} = P_c \left[\frac{1 - \Phi_d}{1 + 0.5\Phi_d} \right] \quad (4)$$

At the other extreme, if the dispersed phase has extremely high permeability ($P_d \rightarrow \infty$), the Maxwell equation simplifies to:

$$P_{\text{MMM}} = P_c \left[\frac{1 + 2\Phi_d}{1 - \Phi_d} \right] \quad (5)$$

Fig. 5 compares experimental data for CO_2 and N_2 permeance of the TFN membranes with the limiting cases of the Maxwell model, assuming the effective thickness of the active layer does not vary significantly with filler loading. It can be seen that the experimental data fall close to the upper limit, demonstrating that the filler provides high permeability pathways for gas transport. The Maxwell model gives a good description of the behaviour even at high loadings where it would not normally be expected to apply. Fig. 6 shows similar plots for CO_2 and N_2 permeability of self-standing MMMs, demonstrating that the performance is close to the Maxwell upper limit over the range of filler loadings achievable.

3.3.2. Effect of ageing on permeance and selectivity

One of the most significant issues for membrane gas separations with PIMs and other high free volume glassy polymers is that of physical ageing; that is, changes in properties that occur over time, arising

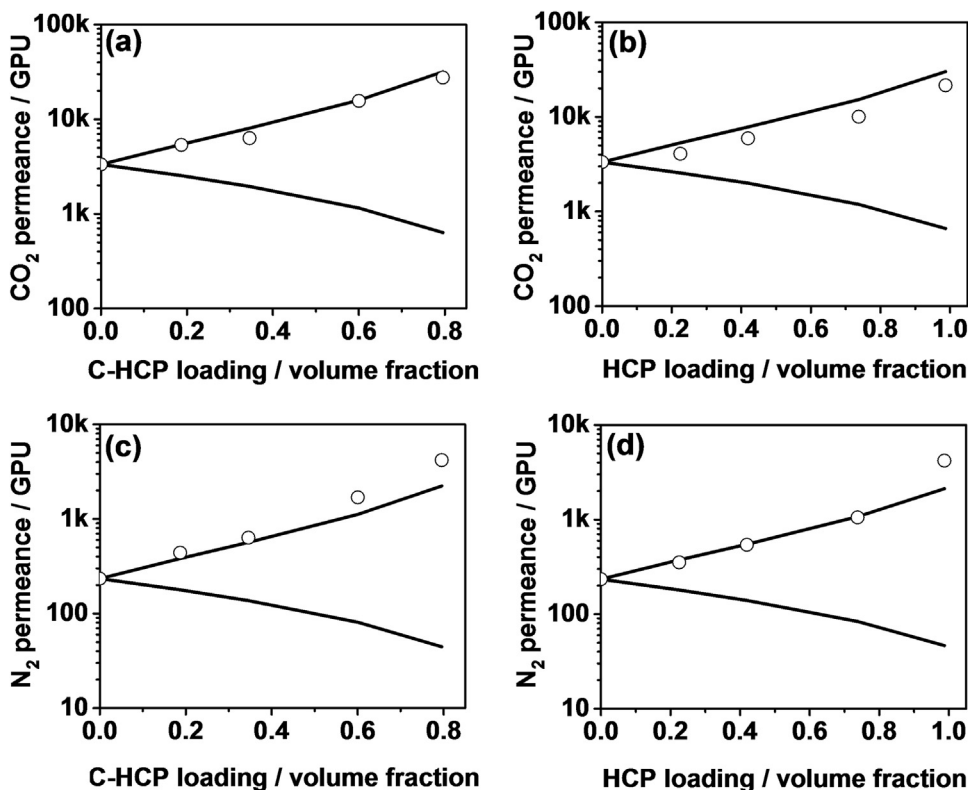


Fig. 5. Dependence of (a, b) CO_2 permeance and (c, d) N_2 permeance on filler loading for (a, c) PIM-1/C-HCP and (b, d) PIM-1/HCP TFN membranes. The open circles represent experimental data and the lines correspond to the predictions of the Maxwell model for the limits of an impermeable filler ($P_d = 0$, lower line) and a very highly permeable filler ($P_d \rightarrow \infty$, upper line).

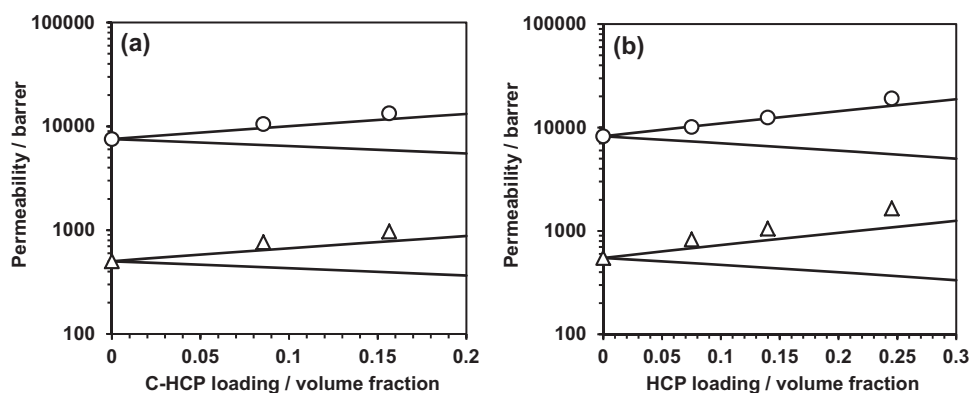


Fig. 6. Dependence of CO₂ permeability (○) and N₂ permeability (△) on filler loading for (a) PIM-1/C-HCP and (b) PIM-1/HCP based self-standing, ethanol-treated MMMs. The solid lines correspond to the predictions of the Maxwell model for the limits of an impermeable filler ($P_d = 0$, lower line of each pair) and a very highly permeable filler ($P_d \rightarrow \infty$, upper line of each pair).

from the non-equilibrium nature of the glassy state. For a thick, self-standing membrane, measurable reductions in permeability may occur over very long timescales (> 4 years) [44]. These effects can be at least partially reversed by an alcohol treatment (immersion in methanol or ethanol overnight, then allowing the alcohol to evaporate), and self-standing membranes are commonly studied after an alcohol treatment to reset the ageing clock. However, such treatments often cannot be applied to thin film composite membranes, because they may lead to delamination of the selective layer. Physical ageing, while leading to a loss of permeability, is often accompanied by an increase in selectivity, and in favourable cases aged membranes may have positive advantages for gas separation, providing that the initial membrane permeance is high enough. The rate of physical ageing depends on film thickness, being much more rapid in very thin films than in thick films [45–48]. Harms *et al.* [49] used depth-resolved positron annihilation lifetime spectroscopy to investigate free volume changes over time in PIM-1 films of various thicknesses. They concluded that in films with thickness $< 1 \mu\text{m}$, ageing is nearly complete after 3 months, whereas for films with thickness $> 1 \mu\text{m}$, ageing continues even after several months. This suggests that stable membranes suitable for commercial

use may be achieved after relatively short ageing times for thin film composite membranes with very thin active layers: indeed, the long-term stability of the support may be of greater concern than changes to the selective layer. Here we sought to confirm the timescale over which ageing effects are significant for TFN membranes, and to investigate the performance that can be achieved in aged membranes.

Fig. 7 shows the changes in CO₂ permeance and CO₂/N₂ selectivity over time for PIM-1/C-HCP and PIM-1/HCP TFN membranes. It can be seen that during the first week of ageing there is a substantial loss of permeance accompanied by an increase in selectivity, with more moderate changes occurring over the following few weeks. In contrast, it can be seen in Fig. 8 that after six months the transport properties of self-standing MMMs continue to show significant changes with time. This is consistent with the conclusions of Harms *et al.* [49].

Bernardo *et al.* [44] have shown that ageing in PIM-1 mainly affects the diffusion coefficient for permanent gases, and that molecules with larger kinetic diameter are affected more by physical ageing than smaller molecules. The kinetic diameters of N₂ and CO₂ are 3.64 Å and 3.3 Å, respectively [50], so the diffusion of N₂ is more restricted and selectivity improves on initial ageing. This may be reinforced by a

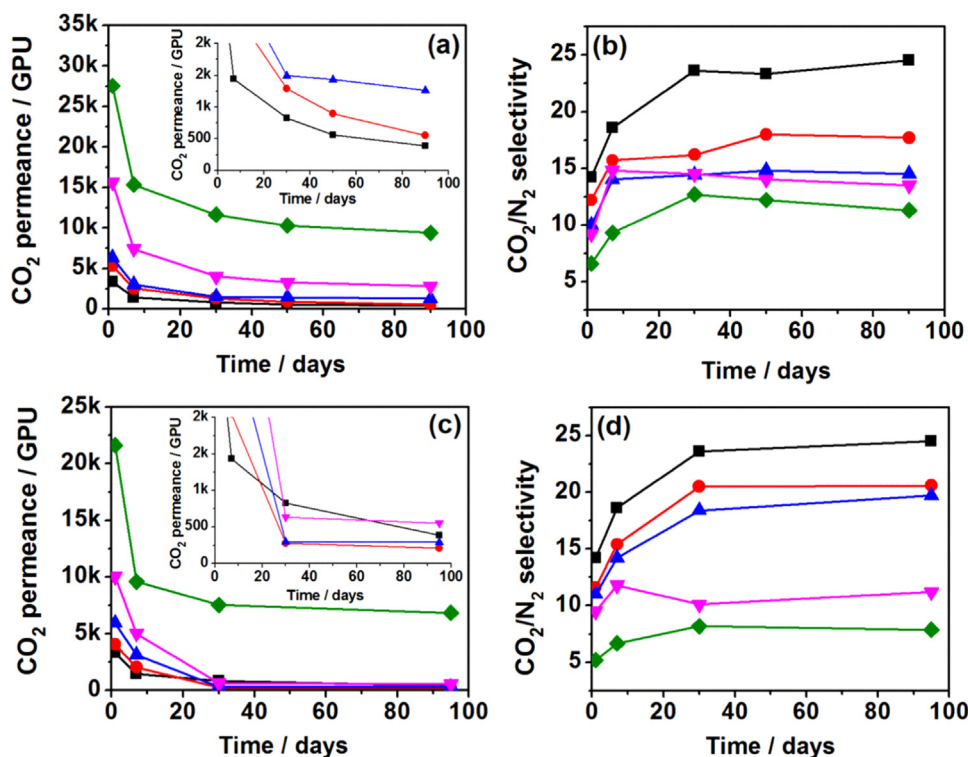


Fig. 7. Changes in (a, c) CO₂ permeance and (b, d) CO₂/N₂ selectivity of TFN membranes over time with (a, b) C-HCP as filler and (c, d) HCP as filler, at filler loadings of 0 wt% (■), 10 wt% (●), 20 wt% (▲), 40 wt% (▼) and 60 wt% (◆).

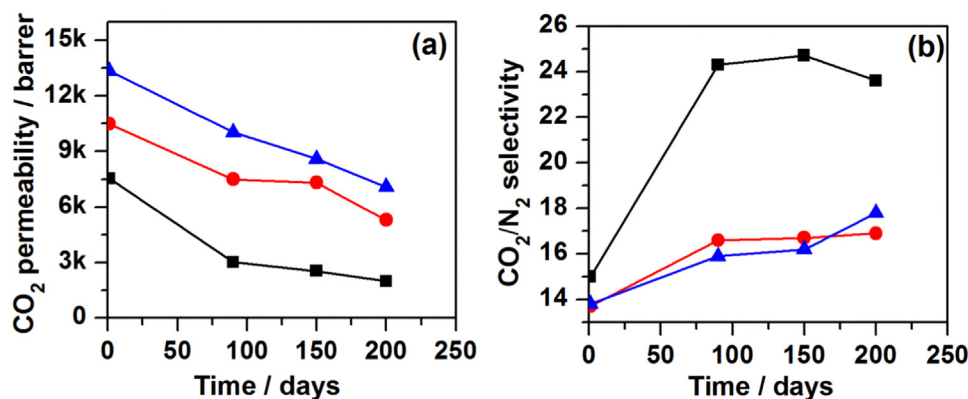


Fig. 8. Changes in (a) CO₂ permeability and (b) CO₂/N₂ selectivity of self-standing ethanol-treated PIM-1/C-HCP MMMs over time, with filler loadings of 0 wt% (■), 4.76 wt% (●) and 9.1 wt% (▲).

favourable sorption term for CO₂. For aged PIM-1/C-HCP TFN membranes, reasonable selectivity can be achieved in combination with very high permeance, e.g., a TFN membrane with 60 wt% C-HCP after 90 days has CO₂ permeance > 9300 GPU with a CO₂/N₂ selectivity of ~ 11.

A Robeson plot [12] of selectivity against permeability provides a useful basis for comparing the performance of different membrane materials and assessing whether ageing has a positive effect (e.g., leading to performance further above the upper bound). Fig. 9 compares data for TFN membranes from this work with data for self-standing MMMs. For TFN membranes, the gas permeances were converted to permeabilities by multiplying by the average thickness of the selective layer as measured by SEM. It is noteworthy that PIM-1/C-HCP TFN membranes at high loadings exceed the 2008 upper bound while exhibiting very high apparent permeabilities, and exhibit comparable performance to recently reported highly permeable PIMs (PIM-TMN-Trip and PIM-TMN-SBI [51]), showing considerable promise for CO₂ separation.

Fig. 10 compares the CO₂ permeation properties of two TFN membranes from this work with data from the literature for other thin film composites. It is clear that PIM-1/C-HCP TFN membranes offer exceptional permeance. Although the selectivity of the best performing membrane reported here (PIM-1/C-HCP, 60 wt%, CO₂/N₂ selectivity ~

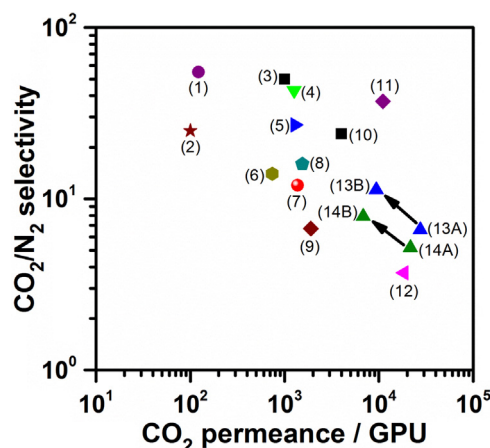


Fig. 10. Summary of the CO₂ permeation properties of selected TFN membranes presented in this work, in comparison with data for other thin film composites. (1) PEBAX1657/PEG [54], (2) commercial natural gas membrane [13], (3) Polaris-1™ [13], (4) PEG based UFC membrane [55], (5) PDA-PEI/SiO₂ [17], (6) PMDA-ODA [56], (7) Pebax®2533/grafted star polymer [57], (8) BPVE-PFCB [58], (9) PTMSP/PAF [59], (10) Polaris-3™ [18], (11) PIM-1/f-MWCNT [60], (12) Cross linked PTMSP [61], (13A-B) PIM-1/C-HCP TFN membrane (60 wt%, A: 1 day, B: 90 days), (14A-B) PIM-1/HCP TFN membrane (60 wt%, A: 1 day, B: 90 days).

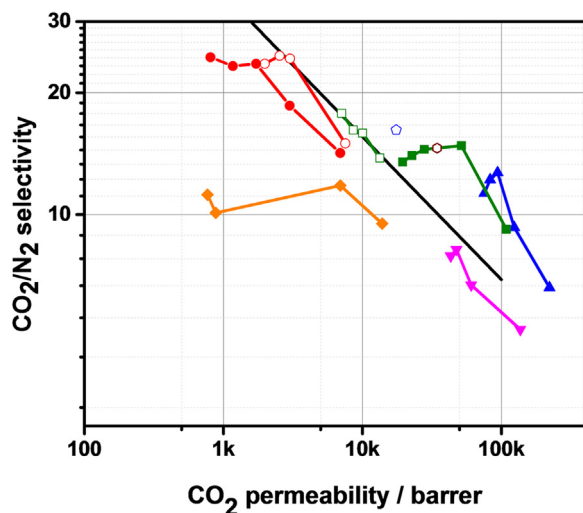


Fig. 9. Robeson plot of ideal CO₂/N₂ selectivity against apparent CO₂ permeability showing Robeson's 2008 upper bound (solid line) and experimental data for TFN membranes of PIM-1 (●), PIM-1/C-HCP 40 wt% (■), PIM-1/C-HCP 60 wt% (▲), PIM-1/HCP 40 wt% (◆) and PIM-1/HCP 60 wt% (▼) after various aging times (1→90 days), and for self-standing ethanol treated MMMs of PIM-1 (○) and PIM-1/C-HCP 10 wt% (□) after various aging times (1→90 days), and high performing PIMs, PIM-TMN-Trip (◐) and PIM-TMN-SBI (◑) [51].

11, $K(\text{CO}_2) > 9300$ GPU) is lower than that of the POLARIS-3 membrane (CO₂/N₂ selectivity ~ 22, $K(\text{CO}_2) \sim 4000$ GPU) [18], it shows significantly higher permeance. There is scope to improve the selectivity of PIM-based TFN membranes, as indicated by the higher selectivities of aged self-standing MMMs, as well as to further enhance permeance by forming even thinner selective layers. A key difference between the TFN membranes and the self-standing MMMs reported here is that solvent evaporation is extremely rapid when CHCl₃ is used as a solvent for dip-coating to form a TFN membrane. By contrast, very slow evaporation conditions are employed when solution casting to form self-standing MMMs. Future work will explore ways of controlling the formation of the selective layer in a TFN membrane. It is also important to note that flue gas for coal-fired power plants contains 3–4% water vapour and trace amounts of impurities such as SO₂ [52]. It is known that the presence of water vapour can cause a reduction in the CO₂ separation performance through competitive sorption and water clustering effects, as the water molecules in the membrane occupy free volume that would otherwise be occupied by CO₂ [53]. Thus, the effect of water vapour on CO₂ separation performance of the TFN membrane will need to be explored in the future.

4. Conclusions

Thin film nanocomposite (TFN) membranes, with selective layers of nanoparticulate fillers in the glassy polymer PIM-1, offer exceptional permeance for CO₂ separation. Carbonised hypercrosslinked polystyrene (C-HCP) nanoparticles have higher internal surface area and greater ultramicroporosity than the uncarbonised form (HCP), imparting greater increases in permeance. Very high filler loadings (up to 60 wt%) could be achieved in TFN membranes, but not in self-standing MMMs. The increase in permeance with increasing filler loading was consistent with the predictions of the Maxwell model for a highly permeable filler. For TFN membranes, the most significant effects of physical ageing, which leads to some loss of permeance coupled with an increase in selectivity, are seen within 90 days, whereas self-standing mixed matrix membranes (MMMs) continue to age significantly beyond 200 days. After ageing, TFN membranes show high permeance with reasonable selectivity, (e.g., with 60 wt% C-HCP, $K(\text{CO}_2) > 9300$ GPU, CO₂/N₂ selectivity ~ 11). We believe that this represents a useful design strategy for cost-effective and scalable TFN membranes for gas separations.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.memsci.2018.07.089](https://doi.org/10.1016/j.memsci.2018.07.089). All research data supporting this publication are directly available within this publication and the supporting information, as well as available from the corresponding authors upon reasonable request.

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